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TRANSFORMATION OF OXIDES OF NITROGEN COMPOSITION WHILE SAMPLING--ETC(U)  
1977 G S SAMUELSEN, J N HARMAN

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TRANSFORMATION OF OXIDES OF NITROGEN  
COMPOSITION WHILE SAMPLING COMBUSTION PRODUCTS

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Abstract

Combustion products are regularly sampled to determine the concentration of the major products of combustion as well as the concentration of the pollutant species. Nitrogen oxides are especially susceptible to changes in concentration that may occur during transport from the sampling point to an instrument for quantitative analysis. The present study reviews the range of conditions over which nitrogen oxides are sampled in practice, and the variety of chemical transformations that may occur within probes and sample lines. In addition, experimental data are presented for chemical transformations that occur for mixtures common to stationary source monitoring, namely combustion products mixtures containing oxygen at temperatures ranging from 25°C to 400°C. Transformations in silica and stainless steel (304, 316, 321) tubing are evaluated. 316 and 321 stainless steel are observed to reduce nitrogen dioxide to nitric oxide at temperatures in excess of 300°C, and 304 stainless steel is observed to reduce nitrogen dioxide at temperatures in excess of 100°C. Silica is observed to be passive to chemical transformation over the temperature range evaluated. Total nitrogen oxides (NO<sub>x</sub>) are conserved in all cases.

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common to stationary source monitoring, namely combustion products mixtures containing oxygen at temperatures ranging from 25°C to 400°C. Transformations in silica and stainless steel (304, 316, 321) tubing are evaluated. 316 and 321 stainless steel are observed to reduce nitrogen dioxide to nitric oxide at temperatures in excess of 300°C, and 304 stainless steel is observed to reduce nitrogen dioxide at temperatures in excess of 100°C. Silica is observed to be passive to chemical transformation over the temperature range evaluated. Total nitrogen oxides (NO<sub>x</sub>) are conserved in all cases.

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## Introduction

The exhaust gas composition from anthropogenic sources such as spark-ignited reciprocating automobile engines, compression ignited diesel engines, package and industrial boilers, steam generating power plants, and gas turbine engines is measured to characterize system efficiency and pollutant emission levels. Measurement of the gaseous product composition emitted from a combustion source generally proceeds by extracting a sample for subsequent quantitative analysis. A typical sampling train is illustrated schematically in Figure 1. In order to maintain sample integrity, the sampling system must be evaluated to ensure that the analytical instrumentation receives a sample that truly represents the concentrations existing at the sampling point. Potential sample transformations should be minimized by careful selection of materials contacting sample gases in the physical probe used for sample removal and in the line used to transport the sample to instrumentation.

Of all the significant products of combustion, nitrogen oxides ( $\text{NO}_x$ ) are especially susceptible to chemical transformation. The variety of combustion sources from which nitrogen oxides are emitted is presented in Table I. Shown are the broad ranges of effluent concentrations, sampling temperatures, and mixture ratios that may be encountered in operating systems.

Emission standards from combustion sources for nitrogen oxides are currently proposed or promulgated by the Environmental Protection Agency (EPA) in terms of total nitrogen oxides,  $\text{NO}_x^{1-3}$ .



As a result, emission factors are determined and compiled for mobile sources (e.g. the automobile) and stationary sources (e.g. power plants) in terms of total nitrogen oxide ( $\text{NO}_x$ ). Current emissions inventories do not differentiate between the species of primary interest in the nitrogen oxides family, nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ). Yet the ratio of emissions of nitric oxide ( $\text{NO}$ ) to nitrogen dioxide ( $\text{NO}_2$ ) from combustion sources is of special interest for a number of applications. For example:

- (1) The local air quality impact of nitrogen dioxide ( $\text{NO}_2$ ) from major line sources requires knowledge of the amount of nitrogen dioxide ( $\text{NO}_2$ ) emitted as a primary pollutant.
- (2) Modeling the visibility of plumes from major power plants requires knowledge of the amount of nitrogen dioxide ( $\text{NO}_2$ ) and nitric oxide ( $\text{NO}$ ) emitted as primary pollutants.<sup>6</sup>
- (3) The input to regional oxidant models requires a spatial and temporal geocoded emissions inventory of nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ) emission from mobile and stationary source operation.
- (4) Flame probing in combustion research is conducted to identify mechanisms responsible for the formation of nitrogen oxides. Measurement of the ratio,  $\text{NO}/\text{NO}_2$ , is important to the determination of the chemistry acting.



### Sampling Conditions

The sampling of combustion products from practical devices (utility boilers, package boilers, diesel engines, gas turbine engines, internal combustion engines), experimental devices (gas turbine combustors, combustion tunnels, stirred reactors), and directly from flames is conducted for a variety of reasons including enforcement, combustion characterization, pollutant formation studies, and efficiency optimization. Sampling is conducted at various locations within a given combustion system and over a wide range of temperatures and gas composition. In addition, the mixture sampled can be either oxidizing or reducing depending on the relative amount of oxidizing species (*e.g.*  $O_2$ ) to reducing species (*e.g.* HC, CO) present at the sampling point.

Table I presents a summary of the typical sampling conditions encountered when measuring  $NO_x$  concentrations from combustion sources. In general, the sampling conditions may be classified into three major groups according to the temperature at which the sample is extracted:

moderate	25°C - 600°C
high	600°C - 1200°C
very high	1200°C - 2500°C

*Moderate* temperature probing (25-600°C) is the most frequently encountered. Flue and exhaust gas sampling from stationary and mobile sources occurs in the moderate temperature range. Examples include source sampling of effluents from utility boilers, package boilers, residential furnaces, diesel engines, gas turbine engines, and automobile engines.

*High* temperature probing is experienced in combustion research, especially in studies of secondary (post flame) combustion processes. Care is required to ensure that the reactions are terminated immediately upon extraction of the sample. Aerodynamic quenching (rapid cooling by immediate expansion of the hot gases through a choked orifice) is a common technique used to quench the reactions and freeze the species concentration.

• *Very high* temperature probing is common in flame research. Although flame research has been historically conducted in laboratory systems (premixed flames, diffusion flames, shock tubes, stirred reactors and plug flow reactors), combustion zones in practical combustion systems are now being probed as well.<sup>7,8</sup> Immediate and substantial cooling upon sample extraction is critical to ensure that the active reactions are quenched.

This paper addresses mechanical probing, namely sampling wherein a sample is extracted by a probe and conveyed to an instrument for analysis through a sample line. Excluded from consideration here are molecular beam and optical sampling methods. A review of the transformation reactions that may occur over the broad range of conditions represented by Table I is first presented. Second, experimental evidence of chemical transformation of nitrogen oxides is presented for the condition of oxygen containing atmospheres at moderate temperatures.

#### Chemical Transformation

Various sources of information are available to assist the practitioner in the design of sampling systems for the measurement of nitrogen oxides. The recognition that chemical



transformation of nitrogen oxides can occur while sampling combustion products has prompted (1) a number of investigations that have explored specialized sampling conditions,<sup>9-12</sup> and (2) a few general reviews of the problems associated with sampling nitrogen oxides from combustion sources.<sup>13-17</sup>

Additional information is available from studies conducted to evaluate converter materials for chemiluminescent oxides of nitrogen analyzers,<sup>18-20</sup> and from studies conducted to explore catalysis for potential use in the oxidation of CO in automobile exhaust by O<sub>2</sub> and NO.<sup>21-23</sup>

#### Types of Transformations

Chemical transformation of nitrogen oxides may be of three general types:

OXIDATION:	NO → NO <sub>2</sub>	NO <sub>x</sub> conserved
REDUCTION:	NO <sub>2</sub> → NO	NO <sub>x</sub> conserved
REMOVAL:	NO, NO <sub>2</sub> → N <sub>2</sub>	NO <sub>x</sub> not conserved

NO oxidation and NO<sub>2</sub> reduction reactions change the ratio of NO<sub>2</sub>/NO without changing the total concentration of NO<sub>x</sub>. (The oxidation of NO does produce a species, NO<sub>2</sub>, that is more susceptible to removal by adsorption or absorption). The third transformation type, removal, acts to decrease the total NO<sub>x</sub> concentration. Summaries of the transformation reactions that may be active in the sampling of combustion products are presented in Tables II, III, and IV for homogeneous, heterogeneous, and catalytic reactions respectively. (Although catalytic reactions may be either homogeneous or heterogeneous they are purposefully distinguished here as a separate subset.)



## Homogeneous Reactions

NO Oxidation. The dominant gas phase oxidation reaction of NO is the termolecular combination with molecular oxygen to form nitrogen dioxide NO<sub>2</sub>:



The reaction is important in the moderate temperature range from 25°C to 600°C. The rate of oxidation depends upon the concentration of O<sub>2</sub>, NO, and NO<sub>2</sub>, and decreases with increasing temperature.

NO<sub>2</sub> Reduction. The reverse of reaction (1)



becomes important as temperature increases. The temperature, then, is important in determining which reaction (1 or 2) is dominant. Although a kinetic analysis is required to determine the relative importance of the two reactions as a function of temperature, an equilibrium analysis is effective in describing the potential competition that can occur. For example, results of an equilibrium calculation are presented in Figure 2 as a function of temperature for a range of oxygen containing atmospheres (balance nitrogen). The initial nitrogen oxides concentration (500 ppm NO, 75 ppm NO<sub>2</sub>) used for the calculations represents concentrations typical of those emitted from operating systems. The equilibrium predictions indicate that substantial changes in NO and NO<sub>2</sub> concentrations can occur given sufficient time. At temperatures below 200°C no change occurs unless oxygen is present. When oxygen is present, the NO is oxidized to NO<sub>2</sub>

at low temperatures. At temperatures above 200°C, the equilibrium begins to shift to NO. The reduction of NO<sub>2</sub> to NO approaches completion at temperatures exceeding 600°C. The effect of oxygen on the percent transformed at 600°C is demonstrated by the detailed insert.

Whether chemical transformation, in fact, occurs via reactions (1) or (2) depends upon the rate of the two reactions at the temperatures of interest, the concentration of the reactant species, and the residence time. Uncatalyzed, reaction (1) does not advance sufficiently for typical sampling times (~ 10 sec) and representative reactant species concentration to significantly affect the NO<sub>2</sub>/NO ratio. For example, at 500ppm NO, 75ppm NO<sub>2</sub>, 5% O<sub>2</sub>, balance nitrogen, the rate of NO<sub>2</sub> formation is 0.133ppm/sec at 100°C. At 400°C, the rate falls to 0.014ppm/sec. Even for levels of NO initially at 5000ppm, less than 3% of the NO will be oxidized to NO<sub>2</sub> after 10 seconds.<sup>24</sup> Unless catalyzed, reaction (2) is also too slow at moderate temperatures, relative to typical sampling times (~ 10 sec) to be important. For example, at 500ppm NO, 75ppm NO<sub>2</sub>, 5% O<sub>2</sub>, balance nitrogen, the rate of NO<sub>2</sub> reduction is  $6.25 \times 10^{-9}$  ppm/sec at 100°C and  $6.33 \times 10^{-2}$  ppm/sec at 400°C. At higher temperatures, however, the rate of reduction of the uncatalyzed reaction may be appreciable. For example, the rate of NO<sub>2</sub> reduction at 600°C via reaction (2) is 6.32ppm/sec and at 800°C increases to 112ppm/sec.<sup>24</sup>

The third homogeneous reaction presented in Table II,





(3)

has been identified as potentially active when sampling in the very high temperature range (1200°C to 2500°C). Relatively long residence times and high concentrations of O-atoms are required for the concentration of NO<sub>2</sub> to be significantly reduced.<sup>12</sup>

NO<sub>x</sub> Removal. Meyerson has demonstrated the homogeneous gas-phase removal of NO in the presence of hydrocarbons. Reduction of NO depends in part on maintenance of elevated temperatures (900°C to 1400°C) and careful control of oxygen to minimize the preferential oxidation of hydrocarbon species with oxygen.<sup>25</sup>

#### Heterogeneous Reactions

NO Oxidation. Allen has suggested that reaction (5) may explain the high concentrations of NO<sub>2</sub> observed by various investigators while sampling from flame zones (very high temperatures). The probe acts as a third body in promoting the radical relaxation of O-atoms with NO.<sup>12</sup> Other radical recombination reactions may participate as well.<sup>26</sup> If the radical species are not immediately quenched by the aerodynamic expansion, reaction (3) may dominate to yield a net reduction of NO<sub>2</sub> to NO.<sup>12</sup>

NO<sub>2</sub> Reduction. NO<sub>2</sub> reduction mechanisms have been the subject of numerous studies that address converter design for chemiluminescent NO-NO<sub>x</sub> analyzers.<sup>13-15</sup> The dominant heterogeneous reactions investigated involve the reduction of NO<sub>2</sub> at the surface due to reactions with metals (e.g. vanadium,



tungsten, manganese, molybdenum, and stainless steel) and carbon. The reactions are temperature sensitive and require temperatures in excess of 300°C to significantly advance the reduction of  $\text{NO}_2$ .<sup>18-20</sup> Carbon particulates formed in combustion processes can also participate in the chemical transformation of nitrogen oxides during sample transport. Heterogeneous reactions involving carbon particulates deposited on the walls of sample probes and sample lines can reduce  $\text{NO}_2$  to NO in both overall reducing and overall oxidizing atmospheres.<sup>15,26</sup>

$\text{NO}_x$  Removal. Nitrogen oxides may be removed by heterogeneous reactions at the wall of sampling materials. A dominant heterogeneous  $\text{NO}_x$  removal reaction is wall absorption or adsorption of  $\text{NO}_2$ . This is common with stainless steel, mild steel, and many metals.<sup>13-16</sup>

White and Beddows, among others, have found glass to be passive to the absorption of nitrogen dioxide ( $\text{NO}_2$ ) at ambient temperatures.<sup>27</sup> TFE Teflon has also been evaluated in various studies with conflicting results. White and Beddows<sup>27</sup> found TFE Teflon to be passive at ambient temperature to  $\text{NO}_2$  absorption whereas Trowell<sup>28</sup> and Healy and Urone<sup>29</sup> have observed strong absorption of  $\text{NO}_2$  by TFE Teflon. The fact that conventional  $\text{NO}_2$  permeation tubes are fabricated from FEP or TFE Teflon, and rely for function on the solubility of nitrogen oxides in the polymer lattice, indicate that these materials are not totally passive. The passivity of the TFE Teflon likely depends on the concentration of  $\text{NO}_2$  and the total pressure of the sample.

Absorption in water condensate by reaction (9) is a principal removal mechanism for  $\text{NO}_2$ . Water is a major product of combustion and may condense on the walls of the probe and sampling lines if the probe and lines are not heated above the dew point. Nitrogen dioxide ( $\text{NO}_2$ ) is water soluble and will be removed by absorption if caution is not exercised to maintain the sample above the dew point temperature in probes and sample lines leading to the analytical instrumentation.<sup>13,16,30</sup> Water is purposefully removed in many situations to protect analytical instrumentation, remove a potentially interfering gas, and/or measure the composition of a dry sample. In such cases, special care is required to ensure that  $\text{NO}_2$  is not also removed.<sup>15,17</sup>

Given sufficient time, other heterogeneous reactions may remove  $\text{NO}_x$ . A two-step mechanism is suggested by Brietenbach and Shelef that leads to the removal of NO via the oxidation of surface carbon by gaseous oxygen to carbon monoxide, and the subsequent oxidation of the carbon monoxide by nitric oxide to form  $\text{N}_2$  and  $\text{CO}_2$ .<sup>20</sup> The NO may be reduced directly by carbon as indicated by reaction (11). Both reactions (10) and (11) are of special concern in carbon converters used for chemiluminescent analyzers, and suggest that caution must be exercised in setting and maintaining carbon converter temperatures.

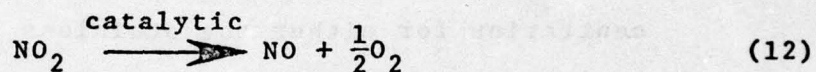
#### Catalytic Reactions

NO Oxidation. Catalysts can promote the oxidation of NO to  $\text{NO}_2$ . Halstead reports that oxidized or heat treated surfaces



can be especially active in oxidizing NO to NO<sub>2</sub>.<sup>13</sup> Additional studies are required to determine the extent of catalytic oxidation of NO for sample times (~ 10 sec) and materials used in sampling nitrogen oxides from combustion effluents.

NO<sub>2</sub> Reduction. In parallel with the NO-NO<sub>x</sub> chemiluminescent converter studies in which various heterogeneous paths for the reduction of NO<sub>2</sub> to NO have been evaluated, catalytic reduction reactions of NO<sub>2</sub> have also been studied.<sup>18,19,20,27,31</sup> Catalytic materials evaluated include stainless steel, gold wool, and quartz. The overall reaction generally regarded as operative in the catalytic reduction of NO<sub>2</sub> is:



Reaction (12) may advance significantly in times typical of sampling (~ 10 sec). The effect of temperature on the dissociation of NO<sub>2</sub> may be implied from Figure 2. Dissociation begins at temperatures exceeding 100°C and is effectively complete at temperatures in excess of 600°C. The oxygen content of the sample will determine the temperature required for complete (> 98%) conversion.

NO<sub>x</sub> Removal. The catalytic reduction of NO by CO has been explored by various investigators for possible application to automobile exhaust control.<sup>21-23</sup> Reduction reactions involving hydrogen and hydrocarbons can occur in parallel with the CO attack on NO, and have also been the subject of recent inquiries.<sup>32,34</sup>

With respect to sampling combustion products, the work

of Halstead is the most definitive statement with respect to the chemical transformation of nitrogen oxides to expect when sampling combustion products containing carbon monoxide. Halstead sampled combustion products from a "Tunnel Mixing Burner" operating on natural gas and air. Two probe materials (stainless steel 210 cm long by 6 mm i.d., and silica tubing, 210 cm long x 4 mm i.d.) were evaluated for lean and rich burn conditions. The temperature at the probe inlet, measured with suction pyrometry, varied between 800 and 1700°C. The temperature of the sample at the outlet was near ambient. The residence time was estimated to be 4 seconds. Under the lean fire conditions, Halstead found no change in NO<sub>x</sub> concentration for either the stainless steel or silica tubing. Changes were observed for rich fire with the stainless steel probe. In particular, the nitrogen oxides (NO<sub>x</sub>) concentration decreased in excess of 90 percent. No effect was observed for the silica.<sup>9</sup> Although the results suggest that important chemical transformation occurs when sampling fuel rich combustion products with stainless steel, important questions remain unanswered. For example, the data are not sufficient to establish the active reactions. Halstead suggests that reaction (14) may be the key to the reduction.<sup>9</sup> However, the extent to which the various reducing species (e.g. carbon monoxide, hydrogen, and hydrocarbons) participate in the reduction reactions cannot be assessed. In addition, the varying temperature along the probe length does not allow determination of the temperature at which the reduction reactions are active.



## Experiment

A variety of reactions may participate in the chemical transformation of nitrogen oxides while sampling combustion products. The assessment of transformations that may occur under conditions experienced when sampling combustion products requires experiments that are specifically designed to identify (1) the chemical transformations, if any, that occur, (2) the extent to which they occur during typical sampling times, and (3) the conditions (*e.g.* sample temperature, sample composition, sample line material) for which they occur.

The present study includes an experiment designed to assess transformation reactions for a specific class of practical combustion devices that operate air-rich--namely boilers, diesel engines, and gas turbine engines. Results are presented for the moderate temperature range typical of exhaust or flue gas sampling. A schematic of the experimental system is shown in Figure 3. The overall design reflects the need to simulate the actual conditions experienced in sampling gaseous combustion products from the variety of sources shown in Table I. Test parameters include carrier gas composition, concentration, and composition of the dopant gases, pre-probe carrier gas temperature, post-probe carrier gas temperature, and probe material.

For the present study, carrier gas is selected from one of three prepared sources of 0, 1, and 5%  $O_2$ , 12%  $CO_2$ , balance  $N_2$ . The carrier gas flow, 4 liters/minutes, is doped with NO

and NO<sub>2</sub> metered from high concentration source cylinders by means of porous sintered metal flow restrictors. The carrier gas enters a silica preheat oven to raise the gas temperature to the probe test temperature. From this point, the doped carrier gas enters the sample probe test section.

The NO and NO<sub>2</sub> input levels are chosen to be 500 ppm NO and 75 ppm NO<sub>2</sub> respectively. These levels simulate NO levels which are typically encountered and NO<sub>2</sub> levels which are representative of those generally thought to exist in combustion source effluents. Sample probe materials evaluated include 304, 316, and 321 stainless steel and silica glass. The length of each sample probe is arbitrarily chosen to be 2 meters. The residence time of the doped carrier gas in the sample probe test section is approximately 1 second for the 4 liters/minute flow rate and 2 meter sample probe length.

The gas temperature within the sample probe is incrementally increased from 25°C to 400°C. Temperatures of the gas stream (T<sub>2</sub> and T<sub>3</sub>) are measured with insulated platinum resistance thermometers centered in the probe bore at the inlet and outlet of the sample probe. The oven temperature is also recorded by a thermocouple located adjacent to the outer diameter of the sample probe.

Gas composition is determined before and after the probe to assess the extent of NO and NO<sub>2</sub> transformation within the 2 meter sample probe segment. Sample lines leading from points 2 and 3 (Figure 3) are short, equal-distant, and made of 1/4 inch diameter



TFE Teflon. Screening tests using varying lengths of TFE Teflon were conducted for the current study to assure that  $\text{NO}_2$  absorption was not a significant factor in the present experiment. However, a systematic evaluation was not conducted and is needed to explain the reported differences in  $\text{NO}_2$  absorption on TFE Teflon.<sup>27-29</sup>

Analysis of  $\text{NO}$  and  $\text{NO}_x$  is conducted with a Beckman Model 951H chemiluminescent oxides of nitrogen analyzer.  $\text{NO}_2$  is determined by difference. The (carbon) converter efficiency is monitored by periodic tests using the methods outlined in the Federal Register.<sup>3</sup>

### Results

The results are presented in Figures 4 and 5 for the silica and the three stainless steel sample probes respectively. The percent change of  $\text{NO}$  and  $\text{NO}_2$  represent the percent change in concentration between sample points 2 and 3. The temperature shown is the gas temperature at sample points 2 and 3.

The results for silica are presented in Figure 4. No significant transformation occurs over the temperature range and the residence time studied. Evidence of  $\text{NO}$  oxidation, proportional to oxygen content, is discernible, however.

The results for 304 stainless steel are presented in Figure 5a. A significant transformation (reduction of  $\text{NO}_2$  to  $\text{NO}$ ) occurs at temperatures in excess of  $100^\circ\text{C}$ . Conversion of  $\text{NO}_2$  to  $\text{NO}$  at elevated temperature by stainless steel is consistent with the results of a variety of studies (Table IV) in which stainless steel has been evaluated for use as the converter material in chemiluminescent nitrogen oxides analyzers. At

temperatures below the catalytically active temperature of 200°C, no significant change is observed. The oxygen content of the mixture has an important impact on the conversion efficiency at the peak temperature evaluated (400°C).

The results for the 316 stainless steel, presented in Figure 5b, indicate a higher temperature for catalytic reduction of NO<sub>2</sub> in comparison to 304 stainless steel. Chemical transformation of nitrogen oxides is negligible for temperatures of 300°C or lower. At 400°C, however, dissociation is nearly 100% complete. The oxygen content of the mixture has a modest impact on the conversion efficiency at the peak temperature evaluated (400°C).

The results for the 321 stainless steel, presented in Figure 5c, show behavior similar to the 316 stainless steel.

The three stainless steels evaluated are similar in the composition of carbon, chromium, and nickel. As shown in Table V, however, 316 stainless steel has molybdenum added to improve corrosion resistance, and 321 stainless steel has titanium added to reduce carbide precipitation. In general, stainless steels have strong resistance to corrosion due to an oxidized layer on the surface. Reducing atmospheres can remove the film and change the passivity. It is likely then that probe history can impact the chemical transformation of nitrogen oxides. Some evidence of this effect has been reported in the literature,<sup>15</sup> but a full assessment has yet to be made.



## Conclusions

Nitrogen oxides may undergo various chemical transformations between the sampling point and the instrument used for detection. The present study has reviewed reactions that may contribute to chemical transformation of nitrogen oxides for the three temperature ranges encountered in practice -- *moderate, high, very high* -- and has addressed experimentally chemical transformation that can occur during moderate temperature combustion source sampling and analysis. In particular, chemical transformation of nitrogen oxides has been explored for those practical combustion devices that operate air-rich, namely boilers, diesel engines, and gas turbine engines.

The conclusions drawn are presented below under two categories: Specific (with respect to the present experiment) and General (with respect to actual source monitoring application). For the conditions explored,

### Specific

- o  $\text{NO}_x$  is conserved in silica and 304, 316, and 321 stainless steel sample probes for the temperature range 25 to 400°C and a residence time of 1 second.
- o Reduction of  $\text{NO}_2$  is observed in 316 and 321 stainless steel sample probes at temperatures exceeding 300°C. In 304 stainless steel sample probes, reduction is observed at temperatures exceeding 100°C.

- o In silica probes, no significant chemical transformation of nitrogen oxides is observed.

#### General

- o Chemical transformation in nitrogen oxides concentration while sampling combustion products should be expected under all conditions.
- o Chemical transformation in nitrogen oxides concentrations are likely to occur when sampling combustion products in excess of 300°C using 316 and 321 stainless steel, and in excess of 100°C using 304 stainless steel sample probes.
- o Chemical transformation in oxides of nitrogen concentration may be effectively prevented by (1) using only silica materials, and (2) exercising appropriate precaution in handling water in the sample.
- o Previous  $\text{NO}_x$ ,  $\text{NO}$ , and  $\text{NO}_2$  data collected at moderate temperatures (25 to 600°C) with stainless steel must be used with caution.
- o Additional information is needed to guide the selection of probe and sample line materials in order to minimize the occurrence of chemical transformation and to determine the extent of chemical transformation under the variety of sampling conditions experienced in practice.



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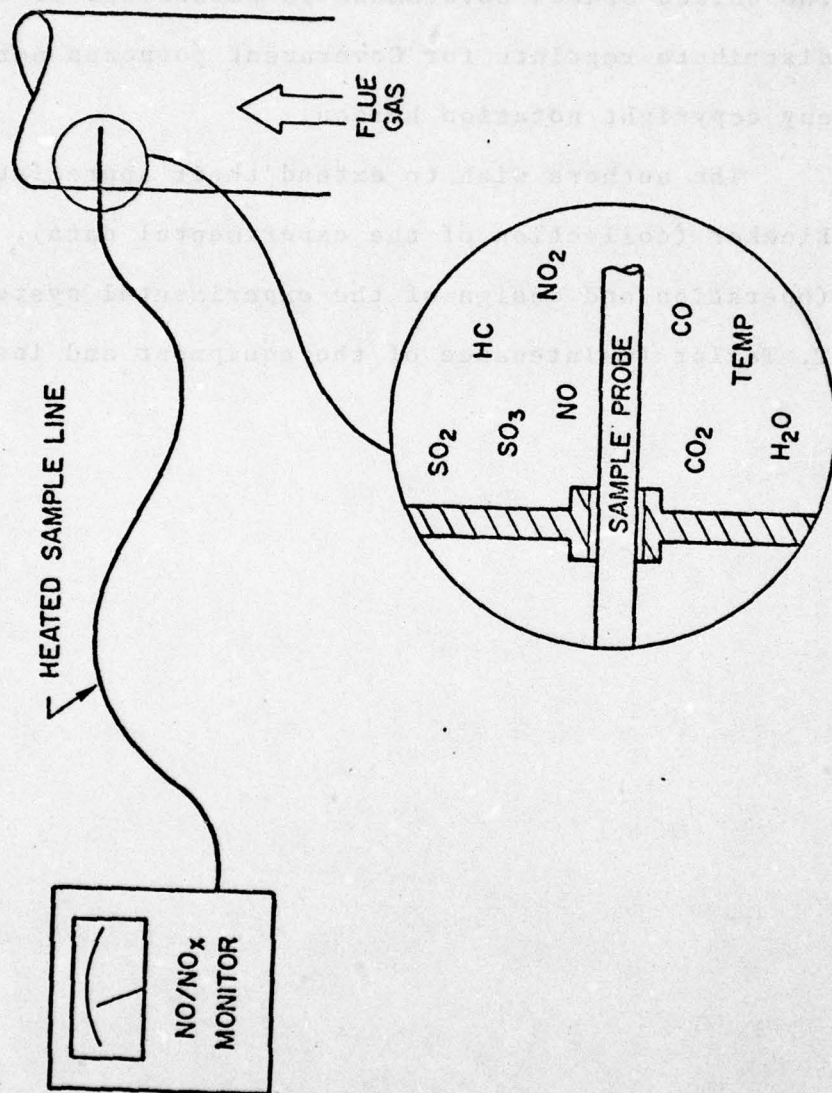


Figure 1 Schematic--Combustion Product Sampling for NO/NO<sub>x</sub>



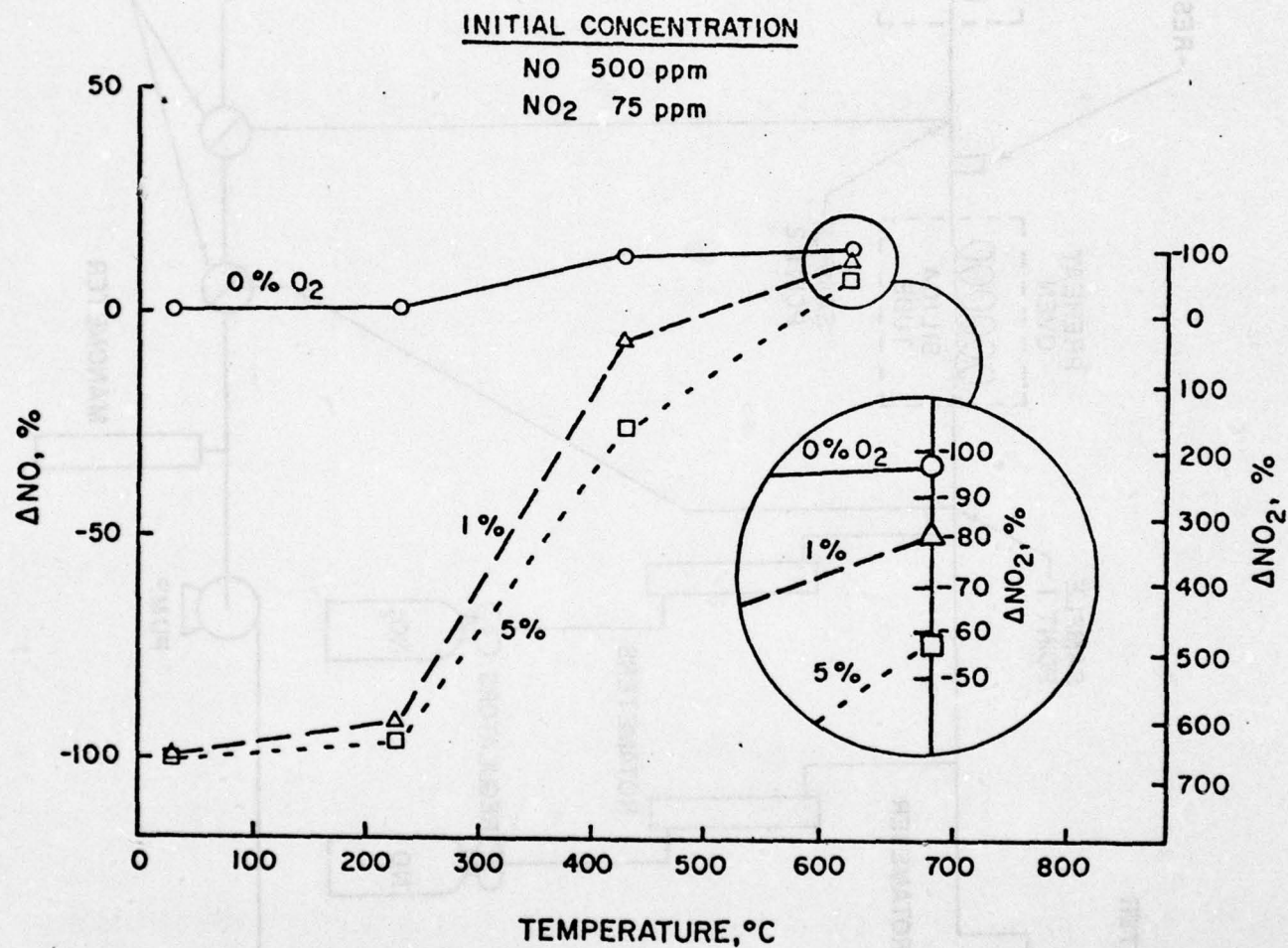


Figure 2 Predicted (Equilibrium) Change of NO and NO<sub>2</sub> Concentration as a function of Temperature at 0, 1, 5% O<sub>2</sub>

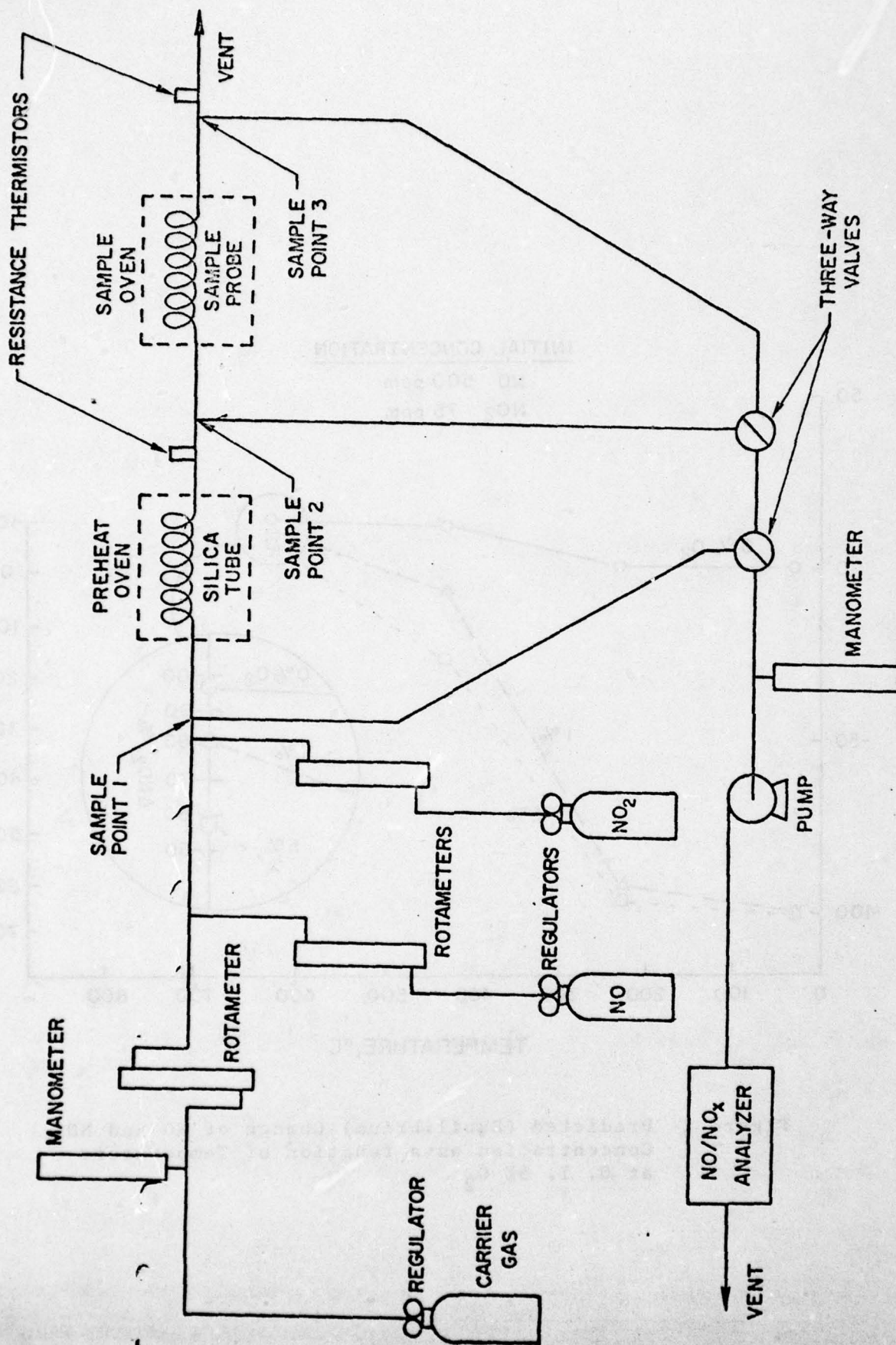


Figure 3 Schematic--Experimental System



Figure 4 Silica Test Probe

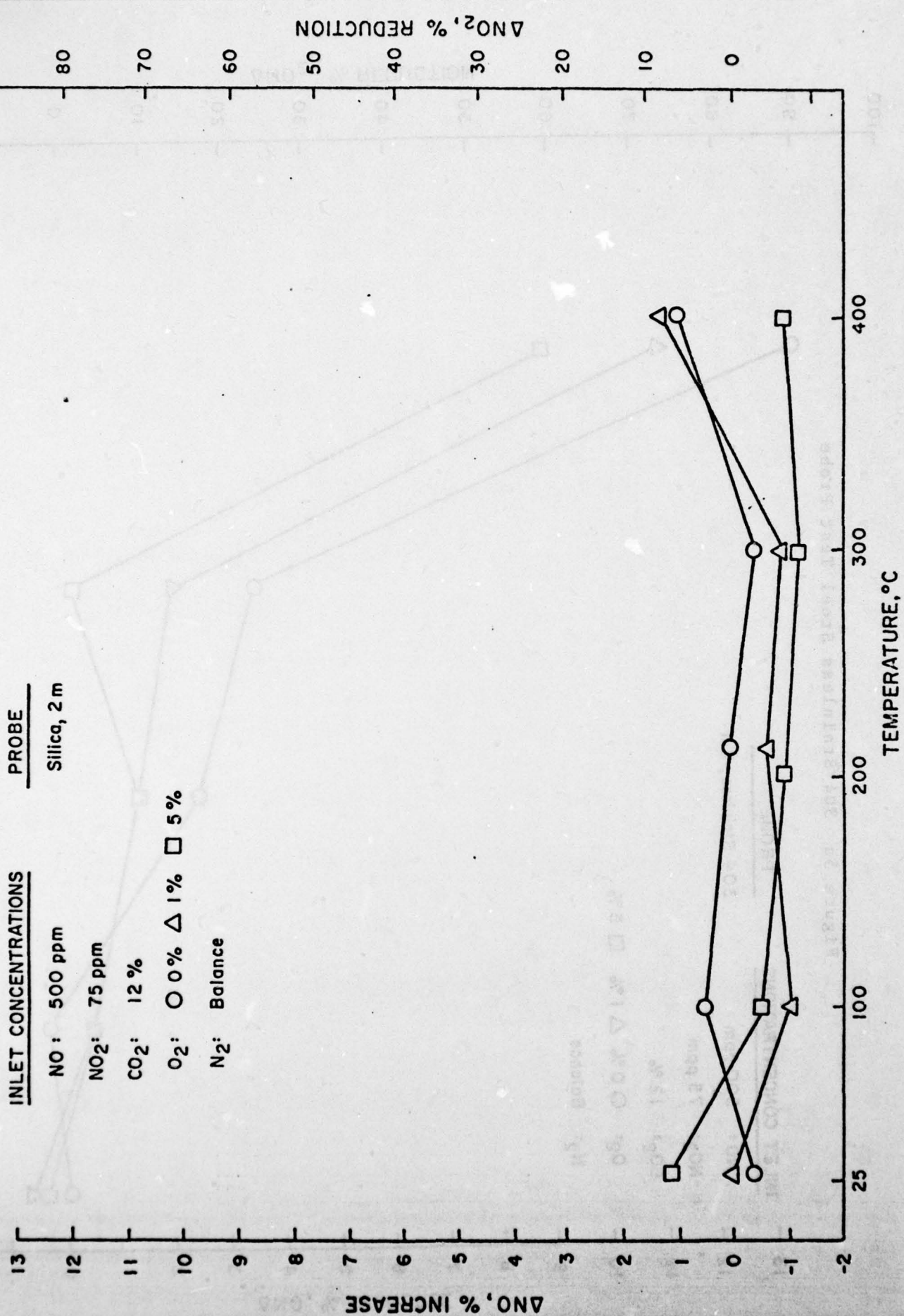


Figure 5a 304 Stainless Steel Test Probe

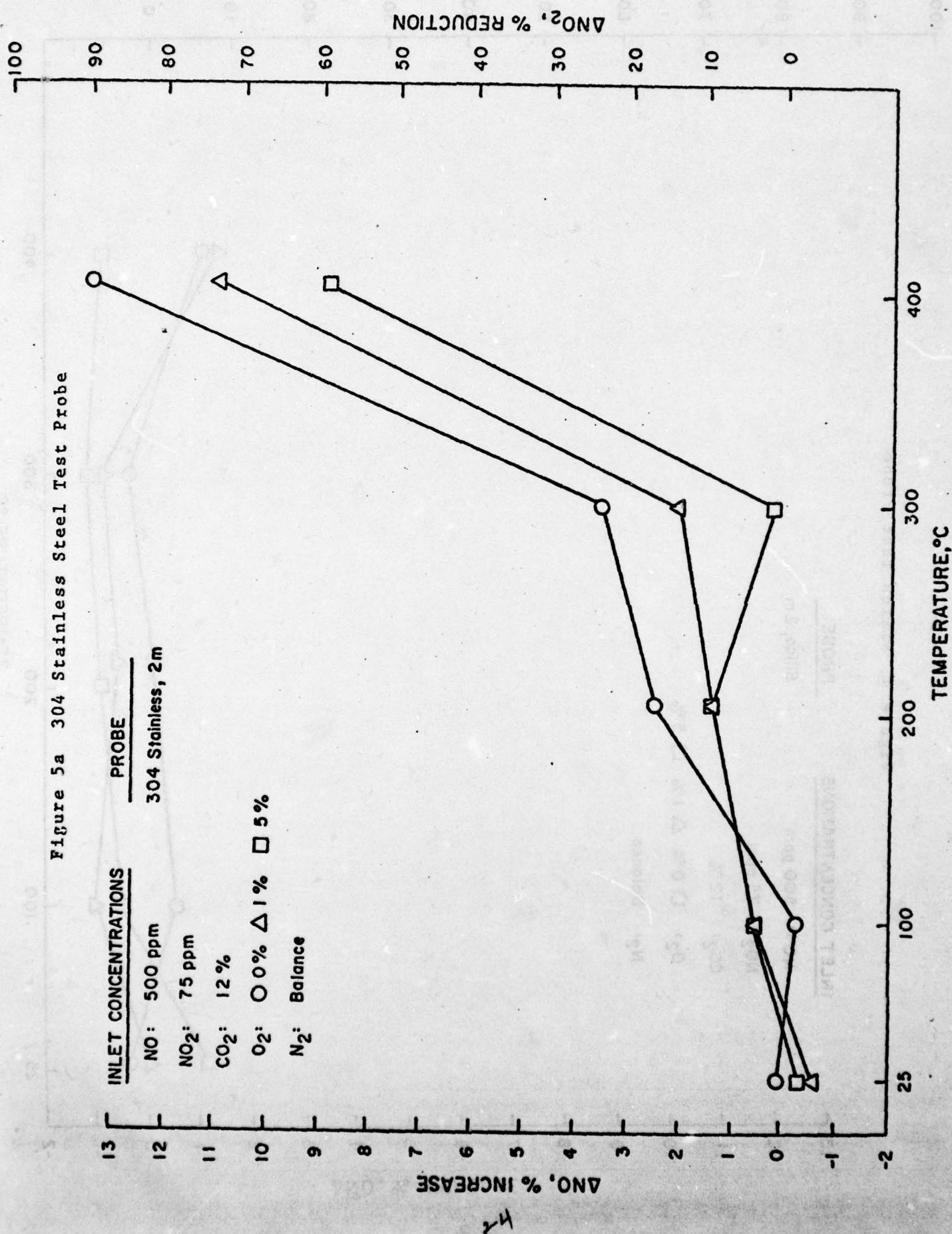




Figure 5b Stainless Steel Test Probe

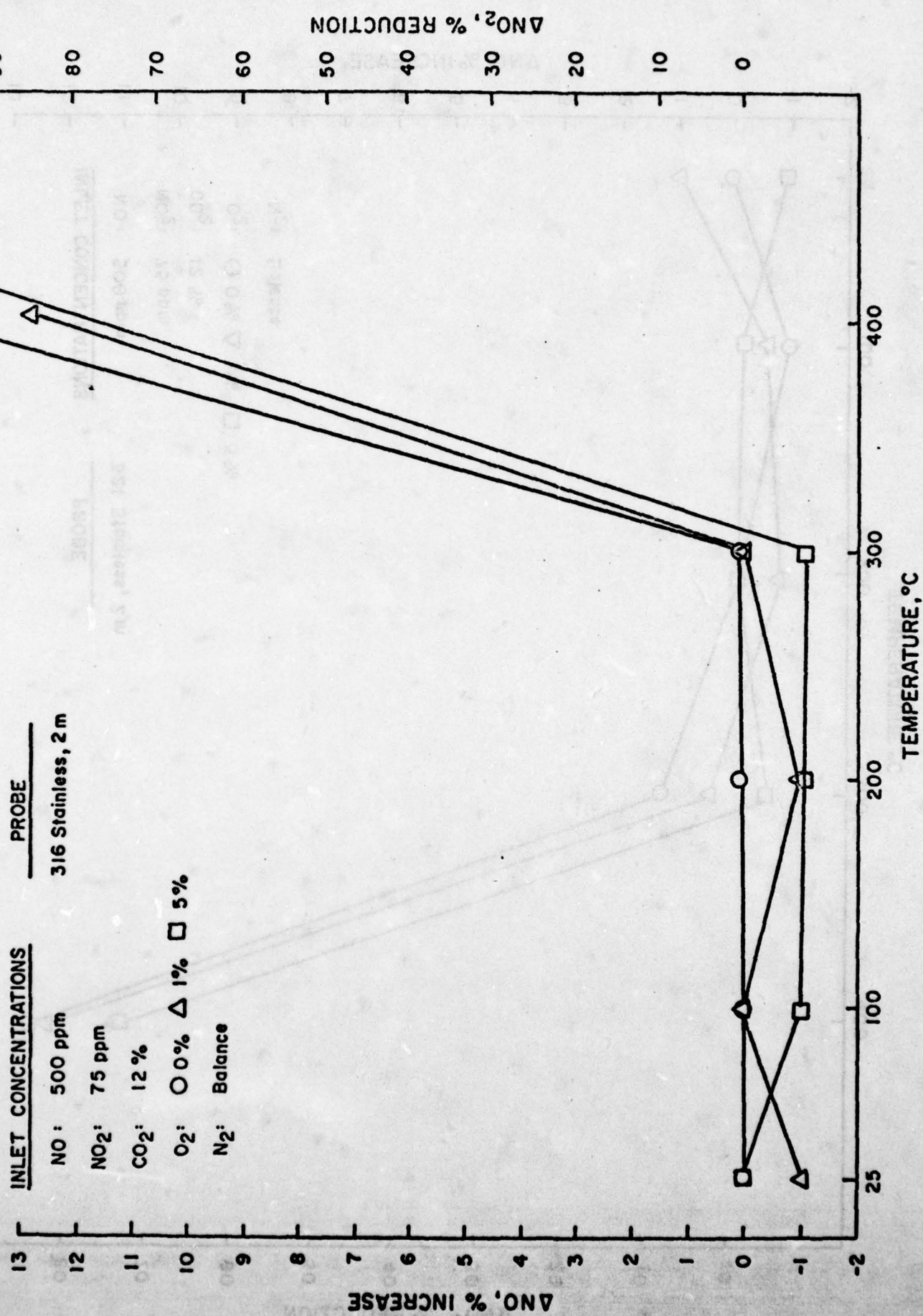
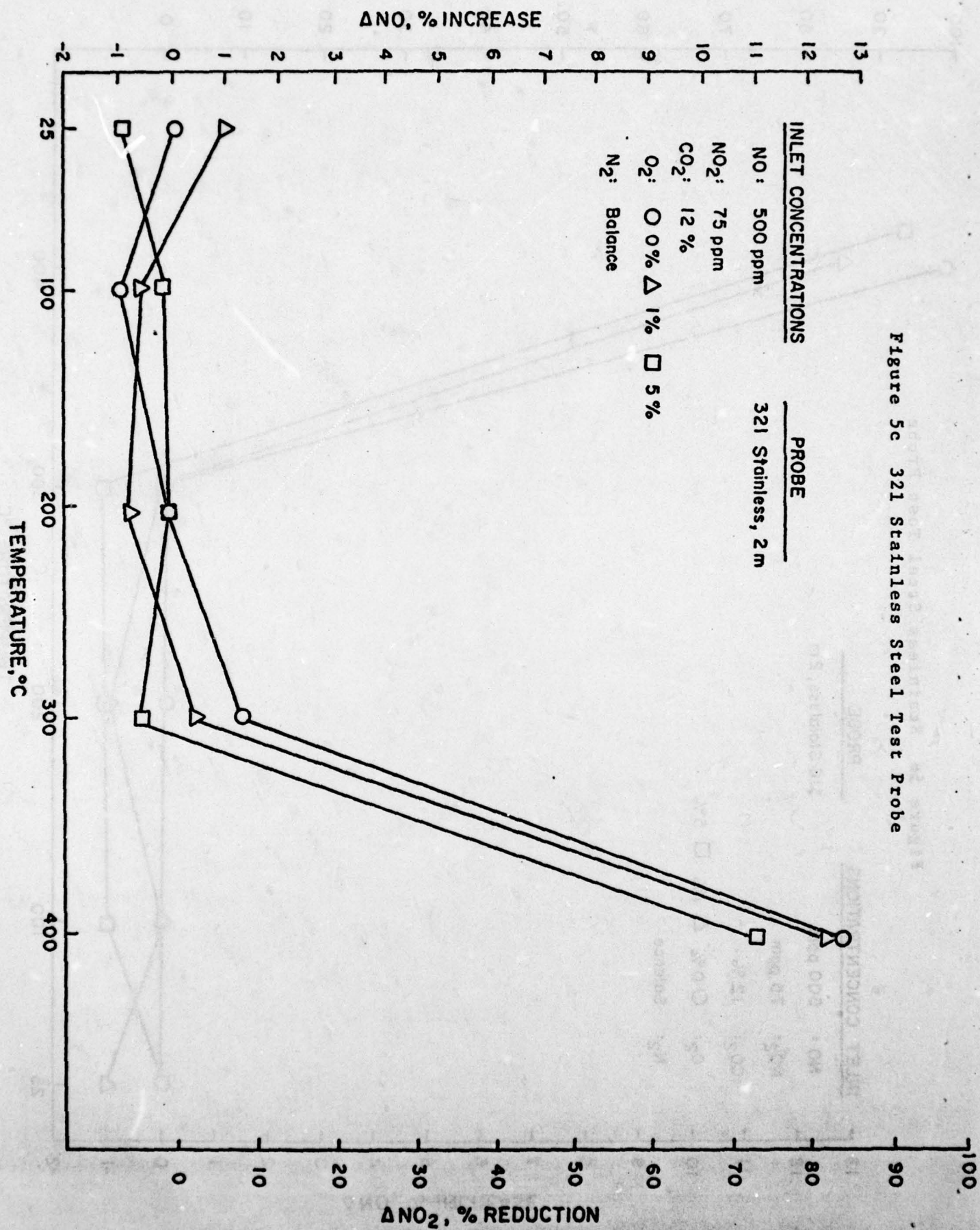


Figure 5c 321 Stainless Steel Test Probe





## REFERENCES

1. "Standards of Performance for New Stationary Sources," Federal Register 36 (247):24876, 23 December (1971).
2. "Control of Air Pollution from Aircraft and Aircraft Engines," Federal Register 38 (136):19088, 17 July (1973).
3. "Control of Air Pollution from New Vehicles and New Motor Vehicle Engines," Federal Register 39 (101):18075, 23 May (1974).
4. "Light-Duty Diesel Powered Trucks," Federal Register 39 (205):37610, 23 May (1974).
5. "Emission Regulation for New Gasoline - Fueled Heavy Duty Engines," Federal Register 40 (40):8482, 27 February (1975).
6. Latimer, D., and G.S. Samuelsen, "Plume Visibility from Major Point Sources," Report No. UCI-ARTR-75-4, UCI Air Quality Laboratory, University of California, Irvine, September (1975).
7. Muzio, L.J., and R.P. Wilson, "Experimental Combustor for the Development of Package Boiler Emission Control Techniques," Report No. R2-73-292a, Environmental Protection Agency, July (1973).
8. Krumwiede, K.R., D.M. Norton, G.W. Johnson, R.E. Thompson, B.P. Breen, and V. Quan, "A Probing Study of NO Formation in the Flame Zone of a 175 MW Gas Fired Utility Boiler," APCA Paper No. 75-23.4, 68th Annual Meeting of the Air Pollution Control Association, June 15-20 (1975).
9. Halstead, C.J., G.H. Nation, and L. Turner, "The Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gas," Analyst 97:55 (1975).
10. England, E., J. Houseman, and D.P. Teixeira, "Sampling Nitric Oxide from Combustion Gases," Combust. Flame, 20:439 (1973).
11. Schefer, R.W., R.D. Matthews, N.P. Cernansky, and R.F. Sawyer, "Measurement of NO and NO<sub>2</sub> in Combustion Systems," Paper No. WSS/CI 73-31, 1973 Fall Meeting of the Western States Section/ The Combustion Institute, El Segundo, California, October (1973).
12. Allen, J.D., "Probe Sampling of Oxides of Nitrogen from Flames," Combust. Flame 24:133 (1975).
13. Halstead, C.J., A.J.E. Munro, "The Sampling Analysis and Study of the Nitrogen Oxides found in Natural Gas/Air Flames," I.G.T/A.G.A. Conference on National Gas Research and Technology, Chicago, Illinois (1971).

14. Halstead, C.J., "Sampling and Analysis of Combustion Products for Nitrogen Oxides," Report No. SIG 71/8, Shell International Gas Limited (1971).
15. Tuttle, J.H., R.A. Shisler, and A.M. Mellor, "Nitrogen Dioxide Formation in Gas Turbine Engines: Measurements and Measurement Methods," Report PURDU-CL-73-06, Grant R-801284, Environmental Protection Agency, December (1973).
16. Allen, J.D., "A Review of Methods of Analysis for Oxides of Nitrogen," J. Inst. Fuel: 123 (1973).
17. Allen, J.D., J. Billingsley, and J.T. Shaw, "Evaluation of the Measurement of Oxides of Nitrogen in Combustion Products by the Chemiluminescence Method," J. Inst. Fuel XLVII:275 (1974).
18. Hodgeson, J.A., J.P. Bell, K.A. Rehme, K.J. Krost, and R.K. Stevens, "Application of a Chemiluminescence Detector for the Measurement of Total Oxides of Nitrogen and Ammonia in the Atmosphere," APCA Paper 71-1067 (1971).
19. Sigsby, J.E., F.M. Black, T.A. Bellar, and D.L. Klosterman, "Chemiluminescent Method for Analysis of Nitrogen Compounds in Mobile Source Emissions ( $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NH}_3$ )," Environ. Sci. Technol. 7 (1):51 (1973).
20. Breitenbach, L.P., and M. Shelef, "Development of a Method for the Analysis of  $\text{NO}_2$  and  $\text{NH}_3$  by  $\text{NO}$ -Measuring Instruments," J. Air Poll. Control Assoc. 23 (2):128 (1973).
21. Baker, R.A., and R.C. Doerr, "Catalyzed Nitric Oxide Reduction with Carbon Monoxide," Ind. Eng. Chem., Process Design Develop. 4 (2):189 (1965).
22. Shelef, M., K. Otto, and H. Gandhi, "The Oxidation of  $\text{CO}$  by  $\text{O}_2$  and by  $\text{NO}$  on Supported Chromium Oxide and Other Metal Oxide Catalysts," Catalysis 12:361 (1968).
23. Ayen, R.J., and Y. Ng, "Catalytic Reduction of Nitric Oxide by Carbon Monoxide," Int. J. Air Water Poll. 10 (1):1 (1966).
24. Baulch, D.L., D.D. Drysdale, and D.G. Horne, Evaluated Kinetic Data for High Temperature Reactions, Volume 2 - Homogeneous Gas Phase Reactions of the  $\text{H}_2$ - $\text{N}_2$ - $\text{O}_2$  System, CRC Press, Cleveland, Ohio, 1973.
25. Myerson, A.L., "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixture," Fifteenth Symposium (International) on Combustion, The Combustion Institute, pp. 1085-1092 (1975).
26. Cernansky, N.P., "Formation of  $\text{NO}$  and  $\text{NO}_2$  in a Turbulent Propane/Air Diffusion Flame," Report No. ME-74-5, Ph.D. Dissertation, Department of Mechanical Engineering, University of California, Berkeley (1974).



27. White, A., and L.M. Beddows, "The Choice of Sampling Tube Material in the Determination of Nitrogen Oxide Concentrations in Products of Combustion," J. Appl. Chem. Biotechnol. 23:759 (1973).
28. Trowell, J.M., "Gas Chromatographic Separation of Oxides of Nitrogen," Anal. Chem. 37:1152 (1965).
29. Healy, T.E., and P. Urone, "Gas Chromatography of Oxidants Using a Flowing Liquid Colorimetric Detector," Anal. Chem. 41:1777 (1969).
30. McMulty, K.J., J.F. McCoy, J.W. Becker, J.R. Ehrenfeld, and R.L. Goldsmith, "Investigation of Extractive Sampling Interface Parameters," Report EPA-650/2-74-089, Environmental Protection Agency, December (1974).
31. Sherwin, E., and C.J. Weston, Chemistry of the Non-Metallic Elements, Pergamon Press, New York (1966).
32. Shelef, M., and H.S. Gandhi, "Ammonia Formation in the Catalytic Reduction of Nitric Oxide. III. The Role of Water Gas Shift, Reduction by Hydrocarbons, and Steam Reforming," Ind. Eng. Chem. Prod. Res. Develop. 13 (1):80 (1974).
33. Klimisch, R.L., and G.J. Barnes, "Chemistry of Catalytic Nitrogen Oxide Reduction in Automobile Exhaust Gas," Environ. Sci. Technol. 6 (6):543 (1972).
34. Klimisch, R.L., and K.C. Taylor, "Ammonia Intermediary as a Basis for Catalyst Selection for Nitric Oxide Reduction," Environ. Sci. Technol. 7 (2):127 (1973).
35. Lyman, T. (ed.), Metals Handbook, Properties and Selection of Metals, Volume 1, American Society for Metals, Metals Park, Ohio, p 564 (1961).
36. Certified Test Report: 304 Stainless Steel, TubeSales (HT 646060), Los Angeles, CA.
37. Certified Test Reports: 316 Stainless Steel, Kilsby Tubesupply Company (HT 220360); 321 Stainless Steel, Kilsby Tubesupply (HT 8040729), Los Angeles, CA.
38. Zuonow, V.A., H.E. Stewart, and E.S. Starkman, "Hydraulically Actuated Combustion Gas Sampling Valve," Rev. Sci. Instr. 39 (12):1820 (1967).
39. Alperstein, M., and R. Bradow, "Combustion Gas Sampling Valve," Rev. Sci. Instr. 36 (7):1028 (1965).
40. Bennethum, J.E., J.N. Mattavi, and R.R. Toepel, "Diesel Combustion Chamber Sampling - Hardware, Procedures and Data Interpretation," SAE Paper 750849, Society of Automotive Engineers (1975).

41. Barrett, R.E., S.E. Miller, and D.W. Locklin, "Field Investigation of Emissions from Combustion Equipment for Space Heating," Final Report, Contract 68-02-0251, Environmental Protection Agency, June (1973).
42. Bartok, W., A. Crawford, and G. Piegari, "Systematic Field Study of NO<sub>x</sub> Emission Control Methods for Utility Boilers," Report No. APTD-1163, Environmental Protection Agency, December (1971).
43. Cato, G.A., and J.M. Robinson, "Application of Combustion Modification Techniques to Control Pollutant Emissions from Industrial Boilers--Phase I," Final Report, Contract 68-02-1074, Environmental Protection Agency, September (1974).
44. Few, J.D., R.J. Bryson, W.K. McGregor, and M.G. David, "Evaluation of Probe Sampling versus an In Situ Optical Technique for Nitric Oxide Concentration Measurement in Combustion Gas Streams," presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, September (1975).
45. Davidson, D.C., and A.F. Domal, "Emission Measurements of a J93 Turbojet Engine," Report No. AEDC TR 73-132, Arnold Engineering Development Center, September (1973).
46. Blazowski, W.S., and R.E. Henderson, "Assessment of Pollutant Measurement and Control Technology and Development of Pollutant Reduction Goals for Military Aircraft Engines," Report No. AFAPL-TR-72-102, Air Force Aero Propulsion Laboratory, November (1972).
47. Elwood, J.H., and R.H. Dieck, "Techniques and Procedures for the Measurement of Aircraft Gas Turbine Engine Emission," APCA Paper 74-90, 67th Annual Meeting, Air Pollution Control Association, Denver, Colorado, June 9-13 (1974).
48. Grossman, J.W., J.H. Slaminski, and A. Licata, "Emission Data and Combustion Calculations for a General Electric PG-5341 Gas Turbine," WSS/CI Paper 74-5, 1974 Spring Meeting of the Western States Section/The Combustion Institute, Pullman, Washington, April (1974).
49. Cernansky, N.P., and R.F. Sawyer, "NO and NO<sub>2</sub> Formation in a Turbulent Hydrocarbon/Air Diffusion Flame," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., pp. 1039-1050 (1975).
50. Merryman, E.L., and A. Levy, "Nitrogen Oxide Formation in Flames," Fifteenth Symposium (International) on Combustion, The Combustion Institute, pp. 1073-1083 (1975).
51. Fenimore, C.P., "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," Thirteenth Symposium (International) on Combustion, The Combustion Institute, pp. 373-380 (1971).



52. Fenimore, C.P., "The Ratio  $\text{NO}_2/\text{NO}$  in Fuel-Lean Flames," Combust. Flame 25:85 (1) (1975).
53. Pompei, F., and J.B Heywood, "The Role of Mixing in Burner-Generated Carbon Monoxide and Nitric Oxide," Combust. Flame 19:407 (1972).
54. Malte, P.C., and D.T. Pratt, "Oxides of Nitrogen Formation for Fuel-Lean Jet-Stirred Carbon Monoxide Combustion," WSS/CI Paper No. 73-37, 1973 Fall Meeting of the Western States Section/The Combustion Institute, El Segundo, California October (1973).
55. Stedman, D.H., E.E. Daby, F. Stuhl, and H. Niki, "Analysis of Ozone and Nitric Oxide by Chemiluminescent Method in Laboratory and Atmospheric Studies of Photochemical Smog," J. Air Poll. Control Assoc. 22 (4):260 (1972).
56. Rosser, W.A., and H. Wise, "Thermal Decomposition of Nitrogen Dioxide," J. Chem. Phys. 24:493 (1956).
57. Stevens, R.K, T. Clark, R. Baumgardner, and J. Hodgeson, "Instrumentation for the Measurement of Nitrogen Dioxide," in Instrumentation for Monitoring Air Quality, ASTM Pub. 04-555000-17, American Society for Testing and Materials (1973).

Table I Sampling conditions for nitrogen oxides.

Source	Typical NO <sub>x</sub> ppm	Sampling Point	Typical Sampling Environment		References	
			Temperature °C	Atmosphere	Examples of NO <sub>x</sub> probing	Prior Studies Relevant to Possible NO <sub>x</sub> Transformations
Internal Combustion Engine	500-4000	Combustion Zone	1300-2400	Reducing	38, 39	--
	500-1000	Engine Exhaust	200-500	Reducing	3, 5	9
Diesel Engine	1000-7000	Combustion Zone	700-2500	Reducing and Oxidizing	40	--
	700-2500	Engine Exhaust	200-500	Oxidizing	4	9
Residential Oil Burners	20-100	Flue Gas	100-300	Oxidizing	41	9
Boilers	200-1000	Combustion Zone	100-1600	Reducing and Oxidizing	7, 8	10, 11, 12
	25-800	Flue Gas	100-300	Oxidizing	1, 42, 43	9
Gas Turbine	1000-8000	Combustion Zone	1300-2700	Reducing and Oxidizing	• 15	--
	25-200	Engine Exhaust	400-1500	Oxidizing	44, 45, 46, 47, 48	9, 15
Flame Research	10-8000	Within Flame	700-2500	Reducing and Oxidizing	49, 50, 51, 52, 53, 54	10, 11, 16



Table II Homogeneous reactions.

Transformation	Reaction	Reference <sup>a</sup>	
		COMB	CONV
<u>NO Oxidation</u>	(1) $2 \text{ NO} + \text{O}_2 \longrightarrow 2 \text{ NO}_2$	9, 13	55
<u>NO<sub>2</sub> Reduction</u>	(2) $2 \text{ NO}_2 \longrightarrow 2 \text{ NO} + \text{O}_2$		19, 56
	(3) $\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$	12	
<u>NO<sub>x</sub> Removal</u>	(4) <sup>b</sup> $\text{NO} + \text{CH} \longrightarrow \text{HCO} + \text{N}$	25	

<sup>a</sup>COMB: Combustion Related Study  
 CONV: Converter Related Study

<sup>b</sup>CH: Hydrocarbon

Table III Heterogeneous reaction,

Transformation	Reaction	Reference <sup>a</sup>		
		COMB	CONV	OTHER
<u>NO Oxidation</u>	(5) $\text{NO} + \text{O} \xrightarrow{\text{wall}} \text{NO}_2$	12		
<u>NO<sub>2</sub> Reduction</u>	(6) $\text{NO}_2 + \text{metal} \xrightarrow{\text{wall}} \text{metal oxide} + \text{NO}$	27	20	
	(7) $\text{NO}_2 + \text{C} \xrightarrow{\text{wall}} \text{CO} + \text{NO}$	26	20, 57	
<u>NO<sub>x</sub> Removal</u>	(8) $\text{NO}_2 \xrightarrow{\text{wall}} \text{absorbed adsorbed}$	9, 13, 16 27		28, 29
	(9) $\text{NO}_2 \xrightarrow{\text{condensate}} \text{absorbed}$	16, 30		
	(10) $\text{C} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{wall}} \text{CO}$		20	
	$\text{NO} + \text{CO} \xrightarrow{\text{catalytic}} \frac{1}{2} \text{N}_2 + \text{CO}_2$			
	(11) $\text{NO} + \text{C} \xrightarrow{\text{wall}} \text{CO} + \frac{1}{2} \text{N}_2$		20	

<sup>a</sup>COMB: Combustion Related Study  
 CONV: Converter Related Study



Table IV Catalytic reactions.

Transformations		Reactions	References <sup>a</sup>		
			COMB	CONV	CAT
<u>NO Oxidation</u>	(12)	$\text{NO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{NO}_2$	13		
<u>NO<sub>2</sub> Reduction</u>	(13)	$\text{NO}_2 \longrightarrow \text{NO} + \frac{1}{2} \text{O}_2$	14	18,19,20, 27,31	
<u>NO<sub>x</sub> Removal</u>	(14)	$\text{NO} + \text{CO} \longrightarrow \text{CO}_2 + \frac{1}{2} \text{N}_2$	9,13		21,22, 23
	(15)	$5 \text{H}_2 + 2 \text{NO} \longrightarrow 2\text{NH}_3 + 2 \text{H}_2\text{O}$			32,33, 34

<sup>a</sup> COMB: Combustion Related Study  
 CONV: Converter Related Study  
 CAT: Catalyst Study

Table V Stainless steel composition.<sup>a</sup>

Specification	S.S. Type	Typical Weight Percent				
		Carbon	Chromium	Nickel	Molybdenum	Titanium
General <sup>35</sup>	304	0.08	18-20	8-12		
	316	0.08	16-18	10-14	2-3	
	321	0.08	17-19	9-12		0.40
Present Study <sup>36,37</sup>	304	0.05	18.12	8.64		
	316	0.004	17.60	12.48	2.72	
	321	0.065	17.75	10.78	0.30	0.47

<sup>a</sup>other elements present include manganese, phosphorus, sulfur, silica, copper